PATENT ABSTRACTS OF JAPAN

(11)Publication number : **07-070222**
(43)Date of publication of application : **14.03.1995**

(51)Int.CI. C08F 4/642
C08F 10/00

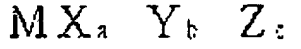
(21)Application number : **05-217598**
(22)Date of filing : **01.09.1993**

(71)Applicant : **IDEMITSU KOSAN CO LTD**
(72)Inventor : **KAWASAKI NOBUO**
WATANABE MASAMI

(54) **OLEFIN POLYMERIZATION CATALYST AND PRODUCTION OF POLYOLEFIN USING THE CATALYST**

(54) OLEFIN POLYMERIZATION CATALYST AND PRODUCTION OF POLYOLEFIN USING THE CATALYST

(57)Abstract:
PURPOSE: To obtain an olefin polymerization catalyst composed mainly of a specific transition metal compound and a specific compound capable of forming an ionic complex, having high activity and capable of producing a polyolefin having high molecular weight in high efficiency.
CONSTITUTION: This catalyst is composed mainly of (A) a transition metal compound of the formula [M is the group 3-5 or lanthanoid metal element of the Periodic Table; X is a (chelating) ligand; Y is a bivalent ligand; Z is a Lewis base, (b) is 1 or 2; (a+2b) is atomic valence of M; (c) is 0-4] such as (B9C2H11)ZrCl2 and (B) a compound capable of forming an ionic complex from the transition metal compound (or its derivative) such as triethylammonium tetraphenyl-borate. A polyolefin is produced by homopolymerizing an olefin or copolymerizing an olefin and other olefins and/or other monomers in the presence of the catalyst.



LEGAL STATUS

[Date of request for examination]	04.07.2000
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3371919
[Date of registration]	22.11.2002
[Number of appeal against examiner's decision of rejection]	

[Date of requesting appeal against examiner's
decision of rejection]
[Date of extinction of right]

- NOTICES *
-

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of polyolefine of having used the catalyst for olefin polymerization, and this catalyst. This invention relates to the approach of manufacturing efficiently the olefin homopolymer which has the above-mentioned property, and a copolymer, in more detail using the catalyst for high activity polymerizations which is the olefin homopolymer of the amount of macromolecules, and the amount of macromolecules, and gives the olefine copolymer of right copolymerization nature, and this catalyst for polymerizations.
[0002]
[Description of the Prior Art] Conventionally, as a high activity soluble olefin-curing catalyst, what consists of combination of a transition-metals compound and aluminoxane is known (JP,58-19309,A, JP,60-217209,A). moreover, ["a journal OBU JI American chemical society (J.Am.Chem.Soc.)" to which it is reported as active species of a soluble olefin-curing catalyst that a cation kind is useful -- the 81st volume, the 81st page (1959), the 82nd volume, the 1953rd page (1960), the 107th volume, and the 7219page(1985)]. moreover, as an example which isolated this active species and was adapted for olefin polymerization "Journal OBU JI American chemical society (J.Am.Chem.Soc.)" The 108th volume, The 7410th page (1986), a ****** No. 502636 [one to] official report, JP,3-139504,A, the Europe public presentation patent No. 468651, etc. as an example which used the organoaluminium compound together to this active species further JP,3-207704,A, the international patent public presentation No. 1723 [92 to], etc. can be mentioned.
[0003] However, the polymer generated with a complex with the cyclopentadienyl system ligand used in these conventional techniques had the trouble that the molecular weight of the polymer obtained was small, when reaction temperature performed a polymerization in an industrial process by efficient 70-200 degrees C or more than it. on the other hand -- "a journal OBU JI American chemical society (J.Am.Chem.Soc.)" -- the 113rd volume, the 1455th page (1991), a U.S. Pat. No. 5,162,466 specification, and a U.S. Pat. No. 5,214,173 specification have composition of a complex with a carborane ligand, and the publication about the polymerization of the olefin using it. And (Cp) (C two B9H11) M (CH3) and [(Cp) (C two B9H11) M]2- (micro-CH 2) (here, Cp is a cyclopentadienyl system ligand and M is transition metals) are illustrated as a complex with this carborane ligand. However, the molecular weight of the polymer obtained using a complex with these carborane ligands and a cyclopentadienyl system ligand is not sufficiently high like the above.
[0004]
[Problem(s) to be Solved by the Invention] This invention is made for the purpose of offering

the approach of manufacturing efficiently the olefin homopolymer which has the above-mentioned property, and a copolymer, using the catalyst for high activity polymerizations which is the basis of such a situation, and is the olefin homopolymer of the amount of macromolecules, and the amount of macromolecules, and gives the olefine copolymer of right copolymerization nature, and this catalyst for polymerizations.

[0005]

[Means for Solving the Problem] this invention persons found out that the purpose could be attained according to the catalyst for polymerizations which uses as a principal component the compound which can form the complex of ionicity from a specific transition-metals compound, and this transition-metals compound or its derivative, as a result of repeating research wholeheartedly, in order to attain said purpose. This invention is completed based on this knowledge.

[0006] That is, this invention is the (A) general formula (I).

MXa Yb Zc ... (I)

the inside of a formula, and M -- the metallic element of the 3-5th groups of the periodic table, or a lanthanoids sequence -- The ligand of the bivalence of the pi-bonding nature in which X contains the ligand or chelate nature ligand of sigma bond nature in, and Y contains a boron atom and a carbon atom at least, Z shows a Lewis base, and when the valence of M and c of 1 or 2, and (a+2b) are the integers of 0-4 and X, Y, and Z of b are plurality, respectively, each Z [each Y / each X and / and] is alike and sets, respectively, and even if the same, they may differ. The catalyst for olefin polymerization which uses the compound which can form the complex of ionicity from the transition-metals compound expressed and (B) this transition-metals compound, or its derivative as a principal component, A list is provided with the manufacture approach of the polyolefine characterized by carrying out copolymerization of homopolymerization or olefins, and/or other monomers for olefins under existence of this catalyst for olefin polymerization.

[0007] It sets for the catalyst for polymerizations of this invention, and is a general formula (I) as a (A) component.

MXa Yb Zc ... (I)

It comes out and the transition-metals compound expressed is used. In the above-mentioned general formula (I), M shows the metallic element of the 3-5th groups of the periodic table, or a lanthanoids sequence. Titanium, a zirconium, a hafnium, vanadium, a niobium, etc. are mentioned as an example of M. X shows the ligand of sigma bond nature, or the sex ligand of a chelate, and alkoxy groups, such as alkyl groups, such as the halogenated compound of a fluorine, chlorine, a bromine, and iodine, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, and an isobutyl radical, a methoxy group, an ethoxy radical, n-propoxy group, an isopropoxy group, an n-butoxy radical, and an iso butoxy radical, etc. are mentioned as an example. the ligand of the bivalence of the pi-bonding nature in which Y contains a boron atom and a carbon atom at least -- being shown -- as an example -- B9 C two H11, B4 C two H6, B3 C two H7, B-2 C2 SH4, BC4 H5, and B-2 C four H6 etc. -- the radical guided from the carborane expressed can be mentioned. In addition, a concrete structure expression is shown in drawing 1 . Z shows a Lewis base. As an example Ether, such as wood ether, diethylether, and a tetrahydrofuran, Ester, such as thioether, such as tetrahydrothiophene, and ethyl benzoate Acetonitrile; Amines, such as nitril, such as a benzonitrile, trimethylamine; triethylamine; tributylamine; N.N-dimethylaniline; pyridine;2, and a 2'-bipyridine; phenanthroline, Triethyl phosphine; Phosphines, such as triphenyl phosphine ethylene; -- butadiene; -- 1-pentene; -- isoprene; -- pentadiene; -- chain-like unsaturated hydrocarbon, such as 1-hexenes and these derivatives, -- benzene; -- toluene; -- xylene; -- cycloheptatriene; -- cyclo-octadiene; -- cyclooctatriene; -- annular unsaturated hydrocarbon, such as cyclo-octatriene and these derivatives, etc. is mentioned. In b, 1 or 2, and (a+2b) show the valence of M, and c shows the integer of 0-4. moreover, when Above X, Y, and Z is plurality, respectively, each Z [each Y / each X and / and] is alike and sets, respectively, and even if the same, they may differ.

[0008] As a transition-metals compound expressed with the above-mentioned general formula (I) For example, (B9 C two H11), ZrCl2 (), [B9] C2 H11ZrMe2 (), [B9 C2] H11Zr2 ()

(CH2 Ph), [B9] C2 H11Zr2 () (OMe), [B9] C2 H11Zr2 () (O-iPr), [B4] C2 H6 ZrCl2, ZrMe (B4 C two H6)2, Zr (B4 C two H6) (CH2 Ph)2, Zr (B4 C two H6) (OMe)2, and Zr (B4 C two H6) (O-iPr)2 etc. -- And the compound with which what 1-4 Lewis bases configurated to these compounds permuted the zirconium by titanium or the hafnium in these further is mentioned. Of course, you may be the analogue of not the thing limited to these but other groups, or the metallic element of a lanthanoids sequence again. In addition, in the above-mentioned compound, in Ph, a phenyl group and Me show a methyl group and iPr shows an isopropyl group. One sort of transition-metals compounds of these (A) components may be used, and may be used combining two or more sorts.

[0009] In the catalyst for polymerizations of this invention, the compound which can form the complex of ionicity from said transition-metals compound or its derivative as a (B) component is used. The ionicity compound which reacts with the transition-metals compound of the ((B-1) A) component, and forms the complex of ionicity as this (B) component, aluminoxane (B-2), and Lewis acid (B-3) can be mentioned. Although anything can be used if it is the ionicity compound which reacts with the transition-metals compound of the aforementioned (A) component, and forms the complex of ionicity as a component, (B-1) The following general formula (II), (III) p q ([Z]-) ([L1-R1] k+) ... (II) ([L2] k+) p q ([Z]-) ... (III) (however, L2 is M2, R2 R3 M3, R43C, or R5 M3.)

L1 among [(II) and a formula (III) Lewis base and [Z]- the anion, i.e., [M1 A1 A2 ..., to which two or more radicals combined non-coordination nature anion [Z1] - with the element - - An]- and here [[Z2]- and here] -- [Z1]- (here -- it is -- M1 -- the 5-15th group element of the periodic table -- the 13-15th group element of the periodic table is shown preferably.) A1 - An A hydrogen atom, a halogen atom, the alkyl group of carbon numbers 1-20, the dialkylamino radical of carbon numbers 2-40, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, the aryloxy group of carbon numbers 6-20, the alkyl aryl radical of carbon numbers 7-40, the arylated alkyl radical of carbon numbers 7-40, the halogenation hydrocarbon group of carbon numbers 1-20, the acyloxy radical of carbon numbers 1-20, an organic metalloid radical, or the hetero atom content hydrocarbon group of carbon numbers 2-20 is shown, respectively. A1 -An Two or more may form the ring inside. n shows the integer of [(valence of the central metal M1) +1]. [Z2]- the logarithm (electric dissociation exponent) of the inverse number of an acid dissociation constant -ten or less Broensted acid -- the conjugate base of the combination of independent or Broensted acid, and Lewis acid or the conjugate base generally defined as super-strong acid is shown. Moreover, the Lewis base may configurate. Moreover, R1 A hydrogen atom, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, an alkyl aryl radical, or an arylated alkyl radical is shown, and it is R2. And R3 It is a cyclopentadienyl group, a substituent cyclopentadienyl group, an indenyl group or a fluorenyl group, and R4, respectively. The alkyl group, the aryl group, alkyl aryl radical, or arylated alkyl radical of carbon numbers 1-20 is shown. R5 Large annular ligands, such as a tetra-phenyl porphyrin and a phthalocyanine, are shown. In the ionic valence of [L1-R1] and [L2], k is the integer of 1-3 and p is one or more integers and q= (kxp). M2 The periodic table 1-3rds, 11-13, and 17 group element are included, and it is M3. The 7-12th group element of the periodic table is shown.] It can come out and what is expressed can be used suitably.

[0010] Here, it is L1. As an example Ammonia, monomethylamine, an aniline, dimethylamine, diethylamine, N-methylaniline, a diphenylamine, N.N-dimethylaniline, a trimethylamine, triethylamine, tree n butylamine, a methyl diphenylamine, a pyridine, p-BUROMO-N, N-dimethylaniline, p-nitro -Amines, such as N and N-dimethylaniline, Nitril, such as ester, such as thioether, such as phosphines, such as a triethyl phosphine, triphenyl phosphine, and diphenylphosphine, and tetrahydrothiophene, and ethyl benzoate, an acetonitrile, and a benzonitrile, can be mentioned. R1 As an example, hydrogen, a methyl group, an ethyl group, benzyl, a trityl radical, etc. can be mentioned, and it is R2 and R3. As an example, a cyclopentadienyl group, a methylcyclopentadienyl radical, an ethylcyclopentadienyl radical, a pentamethylcyclopentadienyl group, etc. can be mentioned. R4 As an example, a phenyl group, p-tolyl group, p-methoxypheny radical, etc. can be mentioned, and it is R5. Tetraphenylporphine, a phthalocyanine, an allyl compound, metallyl,

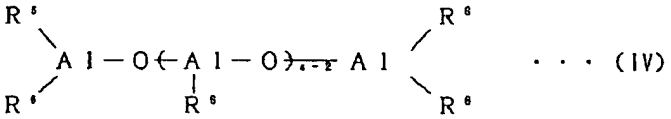
etc. can be mentioned as an example. M2 [moreover,] as an example -- Li, Na, K, Ag, Cu, Br, I, and I3 etc. -- it can mention -- M3 Mn, Fe, Co, nickel, Zn, etc. can be mentioned as an example.

[0011] (Moreover, [Z1]-, i.e., [M1 A1 A2, ... It sets to An] and is M1. As an example, B and aluminum are preferably mentioned for B, aluminum, Si, P, As, Sb, etc.) Moreover, A1 and A2 -An As an example As a dialkylamino radical, a dimethylamino radical, a diethylamino radical, etc., As an alkoxy group or an aryloxy group, a methoxy group, an ethoxy radical, an n-butoxy radical, a phenoxy group, etc., As a hydrocarbon group, a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, n-octyl radical, n-ray KOSHIRU radical, a phenyl group, p-tolyl group, benzyl, a 4-t-buthylphenyl radical, 3, 5-dimethylphenyl radical, etc., As a halogen atom, as a fluorine, chlorine, a bromine, iodine, and a hetero atom content hydrocarbon group p-fluoro phenyl group, 3, a 5-difluoro phenyl group, a pentachlorophenyl group, 3 and 4, 5-trifluoro phenyl group, a pentafluorophenyl radical, 3, 5-screw (trifluoromethyl) phenyl group, a screw (trimethylsilyl) methyl group, etc., A pentamethyl antimony radical, a trimethylsilyl radical, a trimethyl gel mill radical, a diphenyl arsine radical, a dicyclohexyl antimony radical, diphenyl boron, etc. are mentioned as an organic metalloid radical.

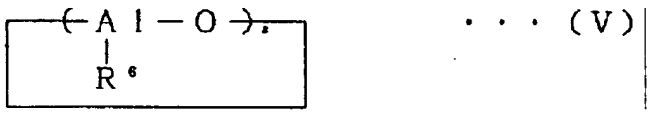
[0012] moreover It is the conjugate base of the combination of the Broensted acid independent not more than -10 or Broensted acid, and Lewis acid [Z2]. - As an example, the anion, i.e., electric dissociation exponent, of non-coordination nature ** trifluoro methansulfonic acid anion () [CF3] SO3-, screw (trifluoromethane sulfonyl) methyl anion, screw (trifluoromethane sulfonyl) benzyl anion, screw (trifluoromethane sulfonyl) amide, and perchloric acid anion (ClO4) -, a trifluoroacetic acid anion () [CF3] CO2-, a hexafluoro antimony anion () [SbF6] -, a fluorosulfonic acid anion () [FSO3] -, a chlorosulfonic-acid anion () [ClSO3] -, a fluorosulfonic acid anion / 5-antimony fluoride (FSO3/SbF5) -, a fluorosulfonic acid anion / 5-fluoride arsenic (FSO3 / AsF5) -, trifluoro methansulfonic acid / 5-antimony fluoride () [CF3] SO3 / SbF5- etc. -- it can mention.

[0013] As an example of the ionicity compound which reacts with the transition-metals compound of such an aforementioned (A) component, and forms the complex of ionicity, i.e., (B-1), a component compound Tetra-phenyl triethyl borate ammonium, tetra-phenyl boric acid tree n-butyl ammonium, tetra-phenyl boric acid trimethylammonium, tetra-phenyl boric acid tetraethylammonium, tetra-phenyl methyl borate (tree n-butyl) ammonium, Tetra-phenyl boric acid benzyl Ammonium, tetra-phenyl boric acid dimethyl diphenyl ammonium, tetra-phenyl boric acid triphenyl (methyl) ammonium, tetra-phenyl trimethyl borate anilinium, tetra-phenyl methyl borate pyridinium, (Tree n-butyl) Tetra-phenyl boric acid benzyl pyridinium, tetra-phenyl methyl borate (2-cyano pyridinium), Tetrakis Triethyl borate ammonium, (Pentafluorophenyl) Tetrakis Boric acid tree n-butyl ammonium, tetrakis (pentafluorophenyl) boric acid triphenyl ammonium, tetrakis (pentafluorophenyl) boric acid tetra--n-butyl ammonium, tetrakis (Pentafluorophenyl) Boric acid tetraethylammonium, tetrakis (pentafluorophenyl) boric acid benzyl (tree n-butyl) ammonium, tetrakis (pentafluorophenyl) methyl borate diphenyl ammonium, tetrakis (Pentafluorophenyl) Boric acid triphenyl (Pentafluorophenyl) Ammonium, tetrakis (Methyl) Methyl borate anilinium, tetrakis (pentafluorophenyl) boric acid dimethyl anilinium, tetrakis (pentafluorophenyl) trimethyl borate anilinium, tetrakis (pentafluorophenyl) methyl borate pyridinium, (Pentafluorophenyl) Tetrakis (pentafluorophenyl) boric acid benzyl pyridinium, tetrakis (pentafluorophenyl) methyl borate (2-cyano pyridinium), Tetrakis (pentafluorophenyl) boric acid benzyl (2-cyano pyridinium), Tetrakis (pentafluorophenyl) methyl borate (4-cyano pyridinium), Tetrakis Boric acid triphenyl phosphonium, tetrakis [screw (3, 5-ditrifluoromethyl) phenyl] boric acid dimethyl anilinium, tetra-phenyl boric acid ferro SENIUMU, tetra-phenyl boric acid silver, tetra-phenyl boric acid trityl, (Pentafluorophenyl) Tetra-phenyl boric acid tetra-phenyl porphyrin manganese, tetrakis (pentafluorophenyl) boric acid ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid (1 and 1'-dimethyl ferro SENIUMU), Tetrakis (pentafluorophenyl) boric acid decamethyl ferro SENIUMU, tetrakis (pentafluorophenyl) boric acid silver, Tetrakis Boric acid trityl, tetrakis (Pentafluorophenyl) A boric acid lithium, tetrakis (Pentafluorophenyl) Sodium borate, tetrakis (Pentafluorophenyl)

(Pentafluorophenyl) Boric acid TEORA phenyl porphyrin manganese, tetrafluoroboric silver, hexafluoro silver phosphate, hexafluoro arsenic ****, perchloric acid silver, trifluoroacetic acid silver, trifluoro methansulfonic acid silver, etc. can be mentioned.
[0014] One sort of ionicity compounds which are this (B-1) component and which react with the transition-metals compound of a ** (A) component, and form the complex of ionicity may be used, and may be used combining two or more sorts. On the other hand, as aluminoxane of a component (B-2), it is a general formula (IV).
[0015]
[Formula 1]



[0016] (-- the inside of a formula, and R6 -- respectively -- becoming independent -- carbon numbers 1-20 -- desirable -- hydrocarbon groups and halogen atoms, such as an alkyl group of 1-12, a cycloalkyl radical, an alkenyl radical, an aryl group, and an arylated alkyl radical, -- being shown -- s -- polymerization degree -- being shown -- usually -- 3-50 -- it is the integer of 7-40 preferably --) -- the chain-like aluminoxane shown and a general formula (V)
[0017]
[Formula 2]



[0018] (-- R6 and s are the same as the above among a formula.) -- the annular aluminoxane shown can be mentioned. What is necessary is for there to be especially no limitation about the means, and just to make it react according to a well-known approach, although the method of contacting alkylaluminum and condensing agents, such as water, is mentioned as a manufacturing method of said aluminoxane. For example, there is an approach to which dissolve ** organoaluminium compound in the organic solvent, add the organoaluminium compound at the beginning at the time of the approach of contacting this in water, and ** polymerization, make trialkylaluminium react to the approach and ** tetra-ARUKIRUJI aluminoxane to which the water of crystallization contained in the approach of adding water behind, ** metal salt, etc. and the water of adsorption to an inorganic substance or the organic substance are made to react with an organoaluminium compound, and water is made to react further. In addition, as aluminoxane, you may be the thing of toluene insolubility. One sort of these aluminoxane may be used and it may be used combining two or more sorts.
[0019] Furthermore, there may not be especially a limit about the Lewis acid of a component (B-3), and an organic compound or a solid-state-like inorganic compound is sufficient. A boron compound, an aluminium compound, etc. are used as an organic compound, and a magnesium compound, an aluminium compound, etc. are preferably used as an inorganic compound. As this aluminium compound, for example, screw (2, 6-G t-butyl-4-methylphenoxy) aluminum methyl, aluminum (1 and 1-BI-2-naphthoxy) methyl, etc. As a magnesium compound, for example, a magnesium chloride, diethoxy magnesium, etc. As an aluminium compound, an aluminum oxide, an aluminum chloride, etc. As a boron compound **, for example, triphenyl boron, tris Boron, tris [3, 5-screw (Pentafluorophenyl) (Trifluoromethyl) phenyl] boron and tris -- [-- Phenyl] boron, trimethyl boron, boron triethyl, tree n-butyl boron, tris (fluoro methyl) boron, tris (pentafluoro ethyl) boron, tris (nona fluoro butyl) boron, tris (2, 4, 6-trifluoro phenyl) boron, (4-fluoro methyl) Tris Boron, tris [3, 5-screw (3, 5-difluoro) Phenyl] boron, a screw (Trifluoromethyl) Fluoro boron, diphenyl fluoro boron, screw (pentafluorophenyl) chloro boron, dimethyl fluoro boron, diethyl fluoro boron, di-n-butyl fluoro boron, pentafluorophenyl difluoro boron, phenyl difluoro boron,

(Pentafluorophenyl) Pentafluorophenyl dichloro boron, methyl difluoro boron, ethyl difluoro boron, n-butyl difluoro boron, 3 fluoride boron, etc. are mentioned. One sort of these Lewis acid may be used, and it may be used combining two or more sorts.
[0020] The operating rate of (A) catalyst component and (B) catalyst component in the catalyst for polymerizations of this invention (B) when a compound is used as a catalyst component (B-1) a mole ratio -- desirable -- 10:1-1:100 -- more preferably, when the range of 1:1-1:5 is desirable and (B-2) uses a compound still more preferably, 2:1-1:10, and a mole ratio -- desirable -- 1:20-1:10000 -- the range of 1:100-1:2000 is more preferably desirable. the case where a compound is used furthermore (B-3) -- a mole ratio -- desirable -- 10:1-1:2000 -- more -- desirable -- 5:1-1:1000 -- the range of 2:1-1:500 is still more preferably desirable. Moreover, as a (B) component, (B-1), (B-2), and (B-3) can also be used combining independent or two sorts or more. This catalyst for polymerizations may contain the aforementioned (A) component and the (B) component as a principal component, and may contain the (A) component, the (B) component, and the (C) organoaluminium compound as a principal component. Here, as an organoaluminium compound of the (C) component, it is (general formula VI) R7 r AlQ3-r. ... The compound shown by (VI) and (R7 showing the alkyl group of carbon numbers 1-10 among a formula, Q showing a hydrogen atom, the alkoxy group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, or a halogen atom, and r being the integer of 1-3) is used.
[0021] Said general formula (VI) As an example of the compound shown, trimethylaluminum, triethylaluminum, triisopropyl aluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminium chloride, methyl aluminum dichloride, ethyl aluminum dichloride, a dimethyl aluminum fluoride, a diisobutyl aluminum hydride, a diethyl aluminum hydride, ethylaluminium sesquichloride, etc. are mentioned. One sort of these organoaluminium compounds may be used and they may be used combining two or more sorts. the operating rate of the catalyst component (aforementioned [A]) and (C) catalyst component -- a mole ratio -- desirable -- 1:1-1:2000 -- more -- desirable -- 1:5-1:1000 -- the range of 1:10-1:500 is still more preferably desirable. Although the polymerization activity per transition metals can be raised by using (** C) catalyst component, if many [not much], while an organoaluminium compound will become useless, it remains so much in a polymer and is not desirable.
[0022] In the approach of this invention, even if there are few catalyst components, a kind can be supported and used for suitable inorganic support or organic support. as inorganic support -- SiO2, aluminum 2O3, MgO, ZrO2, TiO2, Fe 2O3, B-2 O3, and CaO, ZnO, BaO and ThO2 such mixture, for example, a silica alumina, a zeolite, a ferrite, sepiolite, glass fiber, etc. -- further -- MgCl2 Mg (OC two H5)2 etc. -- a magnesium compound etc. is mentioned. On the other hand, as organic support, polymers, such as a polystyrene and styrene-divinylbenzene copolymer, polyethylene, polypropylene, permutation polystyrene, and polyarylate, starch, carbon, etc. are mentioned, for example. the inside of such support -- especially -- MgCl2, Mg (OC two H5)2, SiO2, and aluminum 2O3 etc. -- it is suitable. The mean particle diameter of support has the range more preferably desirable [moreover,] of 20-100 micrometers 10-200 micrometers preferably 1-300 micrometers.
[0023] According to the manufacture approach of the polyolefine of this invention, homopolymerization of olefins or olefins and other olefins, and/or copolymerization (that is, copolymerization between [of a different kind] olefins, copolymerization with olefins and other monomers, or copolymerization with both olefins of a different kind and other monomers) with other monomers can be suitably performed using the catalyst for polymerizations mentioned above. Although there is especially no limit about these olefins, the alpha olefin of carbon numbers 2-20 is desirable. As this alpha olefin, vinyl aromatic compounds, such as ethylene, a propylene, 1-butene, a 3-methyl-1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecen, 1-tetra-decene, 1-hexa decene, 1-octadecene, 1-ray KOSEN, etc. styrene, p-methyl styrene, isopropyl styrene, and t-butyl styrene, can be mentioned. Moreover, what is necessary is just to select suitably from the above-mentioned olefins about other olefins mentioned above.
[0024] In this invention, one sort of above-mentioned olefins may be used, and it may be used

combining two or more sorts. When performing copolymerization of two or more sorts of olefins, the above-mentioned olefins can be combined with arbitration. the case where the operating rate in that case carries out copolymerization of a propylene, ethylene or ethylene, and the alpha olefin of carbon numbers 3-10 -- the copolymerization ratio (mole ratio) of a propylene, ethylene or ethylene, and the alpha olefin of carbon numbers 3-10 -- usually -- 99.9:0.1 to 0.1:99.9 -- it is preferably chosen in 99.5:0.5 to 75.0:25.0. moreover, as other monomers which may be made to carry out copolymerization of the above-mentioned olefins and other monomers, and are used in this invention in this case For example, a butadiene; isoprene; Chain-like diolefins, such as 1 and 5-hexadiene Norbornene; 1, 4, 5, 8-dimethano - Annular olefins, such as 1, 2, 3, 4,a [4], 5, 8, and 8a-octahydronaphthalene;2-norbornene Annular diolefins, such as norbornadiene, 5-ethylidene norbornene, 5-vinyl norbornene, and a dicyclopentadiene Lactone, such as partial saturation ester, such as an ethyl acrylate and a methyl methacrylate, beta propiolactone, beta-butyrolactone, and gamma-butyrolactone Lactams, such as epsilon caprolactam and delta-valerolactam, an epoxy propane; epoxide, such as 1 and 2-epoxy butane, can be mentioned. In addition, the catalyst for polymerizations of this invention is not only used for the polymerization of said olefins, but it can use it for polymerizations other than olefins.

[0025] In this invention, although especially a polymerization method is not restricted but which approaches, such as a slurry polymerization method, a vapor-phase-polymerization method, a bulk-polymerization method, a solution polymerization method, and a suspension-polymerization method, may be used, a slurry polymerization method and especially a vapor-phase-polymerization method are desirable. About polymerization conditions, -50-200 degrees C of polymerization temperature are -100-250 degrees C usually 0-130 degrees C more preferably. Moreover, for the operating rate of a catalyst to a reaction raw material, a raw material monomer / the above-mentioned (A) component (mole ratio) is 1-108, especially 100-105 preferably. Becoming is desirable. furthermore, polymerization time amount -- usually -- 5 minutes - 10 hours and reaction pressure -- desirable -- ordinary pressure -200 kg/cm2 G -- it is ordinary pressure -100 kg/cm2 G especially preferably. There is a polymerization under hydrogen existence etc. in selection of the class of each catalyst component, the amount used, and polymerization temperature, and a pan as the accommodation approach of the molecular weight of a polymer. When using a polymerization solvent, halogenated hydrocarbon, such as aliphatic hydrocarbon, such as alicyclic hydrocarbon, such as aromatic hydrocarbon, such as benzene, toluene, a xylene, and ethylbenzene, a cyclopentane, a cyclohexane, and a methylcyclohexane, a pentane, a hexane, a heptane, and an octane, chloroform, and dichloromethane, etc. can be used. These solvents may use a kind independently and may combine two or more sorts of things. Moreover, monomers, such as an alpha olefin, may be used as a solvent. In addition, a non-solvent can perform depending on a polymerization method. Thus, although especially the molecular weight of the polymer obtained is not restricted,g of limiting viscosity [eta] (it measures in 135-degree-C decalin) is desirable in 0.1 deciliters /or more, and its g is especially desirable in 0.2-30 deciliters /.

[0026] In this invention, precuring can be performed using said catalyst for polymerizations. Although precuring can be performed by contacting a little olefin for a solid-state catalyst component, there is especially no limit in the approach, and a well-known approach can be used. Although what especially a limit does not have and was illustrated above about the olefin used for precuring, the same thing, for example, ethylene, the alpha olefins of carbon numbers 3-20, or such mixture can be mentioned, it is advantageous to use the same olefin as the olefin used in this polymerization. Moreover, -10-130 degrees C of precuring temperature are -20-200 degrees C usually 0-80 degrees C more preferably. In precuring, inert hydrocarbon, aliphatic hydrocarbon, aromatic hydrocarbon, a monomer, etc. can be used as a solvent. Especially a desirable thing is aliphatic hydrocarbon in these. Moreover, a non-solvent may perform precuring. Especially in precuring, it is desirable to adjust conditions so that 1-10000g of amounts of the precuring product to which 0.2 deciliters /or more of limiting viscosity of a precuring product [eta] (it measures in 135-degree-C decalin) receive per transition-metals component 1 millimol in 0.5 deciliters [g] /or more and a catalystg may be

set especially to 10-1000g.
[0027]
[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.
Example 1 (manufacture of an ethylene-1-octene copolymer)
The temperature up of the temperature of a solution was carried out to 60 degrees C, teaching and stirring 360ml of toluene, 40ml of 1-octenes, and methyl aluminoxane (MAO) 5 millimol at a room temperature under nitrogen-gas-atmosphere mind at the 1l. autoclave which carried out heating reduced pressure drying. Subsequently, it is ZrCl (B9 C two H11)2 at 60 degrees C. The temperature up was carried out to 80 degrees C, adding and stirring [drawing 1 reference] complex 5 micromole. Next, the polymerization was carried out for 1 hour, introducing ethylene continuously eight atmospheric pressures at 80 degrees C. Reaction mixture was supplied to the methanol-solution of hydrochloric acid after reaction termination, and the obtained polymer was dried under reduced pressure after 3 times washing with the methanol. The yield of a polymer (ethylene-1-octene copolymer) was 3.0g, the melting point was 127 degrees C and limiting viscosity [eta] (it measures in a 135-degree C decalin) was 2.80 deciliters/g.
[0028] Example 2 (manufacture of an ethylene-1-octene copolymer)
In the example 1, except having used triisobutylaluminum 1 millimol and [PhMe2 NH] [B(C six F5)4] 5 micromole instead of methyl aluminoxane 5 millimol, the polymerization was performed like the example 1 and 0.06g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 122 degrees C, and limiting viscosity [eta] was 10.04 deciliters/g. .
[0029] It sets in the example 3 example 1, and is a main catalyst TiCl(C two B9H11) 2 Except having changed, the polymerization was performed like the example 1 and 0.26g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 119 degrees C, and limiting viscosity [eta] was 2.1 deciliters/g.
[0030] It sets in the example of comparison 1 example 2, and is a main catalyst Cpz ZrCl2 Except having changed, the polymerization was performed like the example 2 and 65g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 117 degrees C, and limiting viscosity [eta] was 2.80 deciliters/g.
[0031]
[Effect of the Invention] By using the catalyst for olefin system polymerizations of this invention, it is the olefin homopolymer of the amount of macromolecules, and the amount of macromolecules, and the olefine copolymer of right copolymerization nature is obtained efficiently.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
Drawing 1: The concrete structure expression of carborane is shown.

EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.
Example 1 (manufacture of an ethylene-1-octene copolymer)
The temperature up of the temperature of a solution was carried out to 60 degrees C, teaching and stirring 360ml of toluene, 40ml of 1-octenes, and methyl aluminoxane (MAO) 5 millimol at a room temperature under nitrogen-gas-atmosphere mind at the 1l. autoclave which carried out heating reduced pressure drying. Subsequently, it is ZrCl (B9 C two H11)2 at 60 degrees C. The temperature up was carried out to 80 degrees C, adding and stirring [drawing 1 reference] complex 5 micromole. Next, the polymerization was carried out for 1 hour, introducing ethylene continuously eight atmospheric pressures at 80 degrees C. Reaction

mixture was supplied to the methanol-solution of hydrochloric acid after reaction termination, and the obtained polymer was dried under reduced pressure after 3 times washing with the methanol. The yield of a polymer (ethylene-1-octene copolymer) was 3.0g, the melting point was 127 degrees C and limiting viscosity [eta] (it measures in a 135-degree C decalin) was 2.80 deciliters/g.

[0028] Example 2 (manufacture of an ethylene-1-octene copolymer)

In the example 1, except having used triisobutylaluminum 1 millimol and [PhMe2 NH] [B(C six F5)4] 5 micromole instead of methyl aluminoxane 5 millimol, the polymerization was performed like the example 1 and 0.06g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 122 degrees C, and limiting viscosity [eta] was 10.04 deciliters/g. .

[0029] It sets in the example 3 example 1, and is a main catalyst TiCl(C two B9H11) 2 Except having changed, the polymerization was performed like the example 1 and 0.26g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 119 degrees C, and limiting viscosity [eta] was 2.1 deciliters/g.

[0030] It sets in the example of comparison 1 example 2, and is a main catalyst Cpz ZrCl2 Except having changed, the polymerization was performed like the example 2 and 65g of ethylene-1-octene copolymers was obtained. The melting point of this polymer was 117 degrees C, and limiting viscosity [eta] was 2.80 deciliters/g.

CLAIMS

[Claim(s)]

Claim 1: (A) General formula (I)

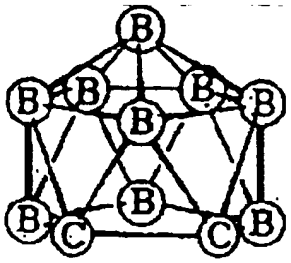
MXa Yb Zc ... (I)

the inside of a formula, and M -- the metallic element of the 3-5th groups of the periodic table, or a lanthanoids sequence -- The ligand of the bivalence of the pi-bonding nature in which X contains the ligand or chelate nature ligand of sigma bond nature in, and Y contains a boron atom and a carbon atom at least, Z shows a Lewis base, and when the valence of M and c of 1 or 2, and (a+2b) are the integers of 0-4 and X, Y, and Z of b are plurality, respectively, each Z [each Y / each X and / and] is alike and sets, respectively, and even if the same, they may differ. The catalyst for olefin polymerization which uses the compound which can form the complex of ionicity from the transition-metals compound expressed and (B) this transition-metals compound, or its derivative as a principal component.

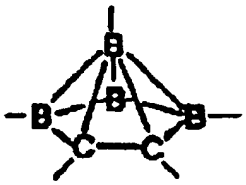
Claim 2: The manufacture approach of the polyolefine characterized by carrying out copolymerization of homopolymerization or olefins, other olefins, and/or other monomers for olefins under existence of the catalyst for olefin polymerization according to claim 1.

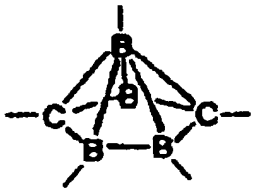
Fig 1:

$B_9C_2H_{11}$

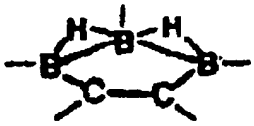


$B_4C_2H_6$

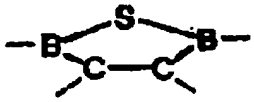




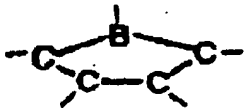
$B_3C_2H_7$



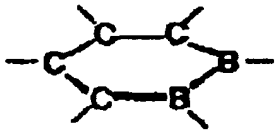
$B_2C_2SH_4$

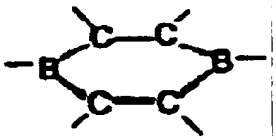


BC_4H_5



$B_2C_4H_6$





[Translation done.]